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The Spectra Product's PH-2 Phenol Instrument was evaluated to determine its applicability to water and wastewaters. The results show that the determinations of phenol in water and wastewaters can be obtained with an accuracy of ±5% in the range of 0.05 to 50.0 ppm and with an accuracy of ±12% in the range of 0.005 to 0.05 ppm. The PH-2 instrument gave more precise results than the 4-AAP methods and can be used to detect para substituted phenols. As with the 4-AAP method, the PH-2 instrument method cannot be used to detect all substituted phenols quantitatively.

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EVALUATION OF INSTRUMENT FOR THE DETERMINATION OF PHENOL IN WATER

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory-Cincinnati conducts research to:

- Develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water. Conduct studies to determine the response of aquatic organisms to water quality.

- Conduct an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

There is an ever-increasing interest in the use of instrumental methods to analyze water and waste samples, whether the resulting data are to be used for research, surveillance, compliance monitoring, or enforcement purposes. Accordingly, the Environmental Monitoring and Support Laboratory has an on-going methods research effort in the development, evaluation, and modification of instrumental methods. This particular report pertains to the evaluation of the PH-2 Phenol Detector. The method has potential routine application for the analysis of phenols in surface waters and domestic and industrial wastes.

Dwight G. Ballinger, Director
Environmental Monitoring & Support Laboratory
Cincinnati

ABSTRACT

This report presents the evaluation of a commercially available ultraviolet spectrophotometer designed specifically for the determination of phenolic compounds in water and wastewater. The analytical procedure is based on the measurement of the bathochromic shift that occurs with phenol when the pH of the solution is changed from pH 4 to pH 12. The method allows for the rapid, sensitive and reproducible analysis of phenols. The time of a single analysis, exclusive of any distillation that may be necessary, is less than five minutes. The results show that the determination of phenols in water can be obtained with an accuracy of ±5% in the range of fifty parts per billion to fifty parts per million and with an accuracy of ±12% in the range of five parts per billion to fifty parts per billion. The results of this study were based on the analysis of a variety of synthetic samples of phenol and of substituted phenols and their mixtures, and of real samples from a number of sampling sites in the local area.

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INTRODUCTION

For many years little initiative was taken to abate the pollution of our environment and the misuse of our natural resources. In fact, communities took the view that the benefits accruing to them from the industries that were polluting the environment outweighed the backlash of pollution environmental degradation. Thus, most communities and governmental agencies were insensitive to the problem and regarded pollution as an unfortunate, but nonetheless acceptable, side effect of industrialization. However, within the past few years, the public has developed a greater cause for concern regarding pollution control and management of the environment. The concern has developed because of the greater public awareness about the growing environmental deterioration and the need to maintain acceptable environmental standards for healthful living of a growing population. As the awareness of the pollution problem has sharpened, it has become clear that people and other sources have been as guilty of pollution of the environment as industries (1,2). However, it is obvious that much of the environmental deterioration is a consequence, directly and indirectly, of the technological advances that have occurred (1). Both population growth and the demand for more goods and services have contributed to the rapid increase in industrialization and technological advances. Thus, the advances in technology and industrialization, with a greater demand of our physical and human resources, have added new dimensions to the problems of controlling further environmental deterioration. Because of public concern, the government now has taken steps to more adequately manage and control our environment by establishing guidelines and regulations to monitor and control pollution and the misuse of our natural resources. The success of these steps depends in a large measure on identifying serious pollutants, measuring their quantities, and developing methods to remove them so that they do not enter the environment (3).

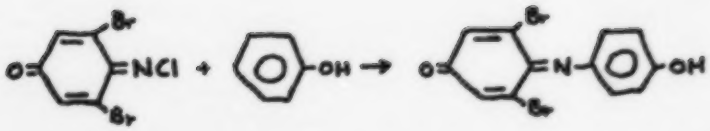
The deterioration of the environment is well illustrated by the exploitation and misuse of our water resources (1,4-6). A cursory examination of many of our water sources clearly demonstrates that they have become more polluted over the years. However, water pollution is of specific concern to everyone for it is our rivers, streams, and lakes that are a major source of food, that are widely used for recreational purposes, and, more importantly, that are sources of drinking water for many of our communities. At the same time, it has been noted that the natural processes which help restore water to its natural condition are hampered by the increase of pollutants that find their way into the streams, lakes, and rivers. While much of the pollution of our water resources has been attributed to industrialization and urbanization, it is predictable that both of these factors will continue to increase in the future. Therefore, better water management is necessary to maintain, protect and upgrade water quality for present and future potential uses by an increasing population and industrialization.

One of the major concerns of the environmental scientist has been the marked increase in the number of organic compounds that find their way into our water sources. Many of these organic pollutants are derived from industrial plants, but agricultural run-off, mine drainage, and domestic wastes contribute a significant share of responsibility. Of the large volume of organic chemicals produced by industry, phenol and phenol derivatives widely used in the manufacture of dyes, polymers, pesticides and pharmaceuticals represent a significant percentage of the organics that find their way into the waste products dumped into our rivers, lakes and streams. These phenols are troublesome in that they are not removed completely in waste treatment plants and thus become the source of offensive odor and taste in drinking water (7-9). Many phenolic compounds found in water are chlorinated during the process of water treatment and become the source of the objectionable odor and taste in water (10). Significantly, for example, it has been reported that chlorphenol produces an unpleasant taste in fish at concentrations of 0.1 microgram per liter (μg/l) (11). Although research has not shown that these phenolic compounds are harmful or a hazard to health at very low concentrations, the odor and taste that they impart to drinking water, even at very low levels, make them serious water pollutants. Thus, the need to monitor and control the amount of phenolic compounds and other organics in water and wastewater is of concern to the environmental scientist.

Analytical chemistry and instrumentation have long played a vital role in the detection and identification of the many pollutants in water. As the number of identifiable pollutants increases and their toxicities are determined, it is necessary that improved techniques be developed to measure the pollutants at much lower levels than available by using present methods. Such analytical methods must be applicable to a variety of water samples and in the presence of a variety of contaminants. Much effort has been undertaken, therefore, in analytical chemistry to improve on the procedures for the analysis of organics, such as phenolic compounds.

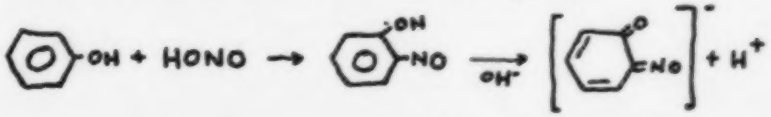
A review of the literature reveals that a number of procedures for the determination of phenolic compounds in water have been studied. It should be noted that, to date, all of the methods depend on the condensation or reaction of some reagent with the aromatic ring of phenol and not with the hydroxyl function of phenol. Unfortunately, many of these procedures have a variety of shortcomings. Thus, there is still a need for a rapid, reliable procedure for the determination of phenolic compounds that is applicable to a wide range of concentrations and types.

One of the early developed and frequently used method for the determination of phenolic substances was that proposed by Gibbs (12). This analytical procedure is based on the reaction of phenolic compounds with dibromoquinone in a buffered alkaline solution to form dibromoindephenol dyes.



The dye is measured colorimetrically at 610-630 nm, and the concentration is determined from a prepared standard curve. Concentrations of phenolic compounds in the range of 0 to 10 parts per million (ppm) can be measured. In the concentration range of 3 to 100 parts per billion (ppb), the dye must be concentrated by extraction with n-butyl alcohol and measured at 670 nm. In this procedure, it has been found that control of pH is critical, because any variation affects color development, as do temperature changes. It should be noted that the procedure requires from 6 to 24 hours for an analysis, because various phenolic compounds react at different rates. Even so, some phenolic compounds, such as p-cresol, do not react in this method. Studies of the technique indicate that the lower concentration limit of phenolic compounds that can be determined is about 50 ppb, and the error in measurement is about 2-3%. However, the problems associated with this procedure have led to a study of others (13-16).

Another method that has been examined is the reaction of phenolic compounds with nitrous acid to form a nitrosophenol.

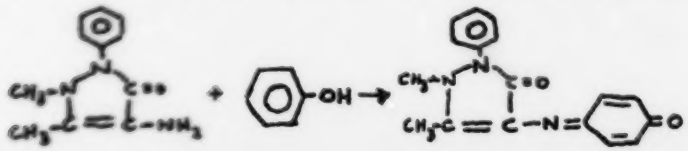


The nitrous compound is then rearranged in an alkaline medium to form a colored quinoid salt, which is measured colorimetrically at 420 nm (16-18). In this procedure, certain amines and inorganic salts interfere somewhat with the development of the color, and up to 24 hours may be required for the analysis. Very few non-phenolic compounds interfere, but it has been found that para-substituted phenolic compounds do react. For low concentration determinations, an extraction procedure is needed to concentrate the phenolic compounds. Again, this procedure has not been widely adopted because of the time requirement and the consistently low results obtained. However, precision of ±1% has been reported for this method.

Recently, gas chromatography and infrared methods of analysis have been developed for determination of phenolic compounds (16, 19-22). Although these methods utilize instrumental procedures found in most laboratories, the cost of the equipment can be prohibitive for many laboratories. In gas chromatography, water samples require the extraction of the organic compounds before the analysis. Thus, considerable time may be consumed in concentrating the organics from the water samples. However, gas chromatography can give reliable data on all types of phenolic compounds, and this procedure is used primarily for the separation and identification of phenolic compounds in the parts-per-million range.

The infrared absorption procedure is based on the ease of bromination of phenolic compounds and the measurement of the shift of the O-H infrared band of the carbon tetrachloride (CCl_4) extracted brominated compound. The shift of the O-H band occurs as a result of hydrogen bonding between the O-H group and the ortho bromine atom. The magnitude of this shift remains constant as long as the bromine substitutes ortho to the O-H group, which means if the di-ortho position is substituted with groups other than bromine, phenol cannot be determined with this method. However, it has been found that this procedure is quite sensitive even in the parts-per-billion range. The limitations of this procedure appear to be the cost of the equipment and that phenol cannot be determined, if steric effects keep them from brominating.

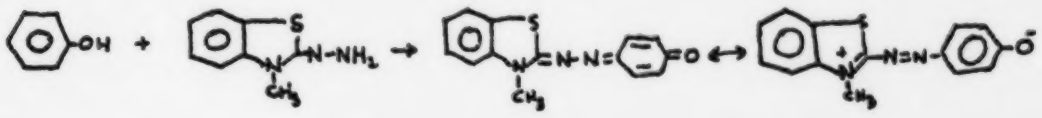
The most commonly used procedure is that developed by Emerson (23-26), which is based on the reaction of phenolic compounds with 4-aminoantipyrine (4-AAP) in an alkaline oxidizing medium to form antipyrine dyes.



The aqueous solution of the dye is measured colorimetrically at 510 nm, and the concentration of phenolic compounds is determined as phenol by comparison with a standard curve. For concentrations in the range of parts per billion, the dye is extracted with chloroform and its absorbance measured at 460 nm. This method has been used routinely in a variety of applications for many years and has been adopted for the determination of phenol by the American Society for Testing and Materials (27) and the American Public Health Association (28). Because of its acceptance as the standard method, it has been examined closely for the effects that variables have on the determination of phenolic compounds. One of the serious disadvantages of this procedure is that phenols having substituents in the para position do not react to give the colored dye. However, it has been found that in the reaction, groups such as halogen, hydroxyl, carboxyl, methoxy, and sulfonic acid are replaced and thus the para substituted phenols react with the 4-AAP. Careful studies have been made of the effect that pH, order of addition, concentration of reactants, temperature, and aging have on the development of the colored dye and on the sensitivity of the determination (16, 29-34). These studies have led to the establishment of a widely used standard procedure which give reproducible and reliable results in the useful range of 2.0 ppm to 20 ppb at an accuracy of ±2%. Frequently, because of turbidity, samples must be distilled before using the method, which adds to the time necessary to obtain an analysis. The time required is, nevertheless, much less than that needed in the methods discussed above; hence it has become the most widely used procedure for a wide variety of analyses.

A recent modification and improvement of the 4-AAP method has been developed by Friestad (35). This method depends on the oxidative coupling

of phenolic compounds with 3-methyl-2-benzothiazoline hydrazone (MBTH).



This method is not as dependent on the availability of the para position in phenols, as the 4-AAP method is, since, if the para position is blocked, the reaction will take place at a free ortho position. The colored compound obtained is measured spectrophotometrically at 520 nm and compared with standard solutions. As with the methods described above, this procedure determines all phenolic compounds as phenol. Better results are obtained by this method than those of the 4-AAP method, and the detection limit is about 5 ppb. Samples of the dye at very low phenol levels are concentrated by extraction with chloroform. Although this method extends the range of phenolic compounds that can be detected and is less subject to interferences than the 4-AAP method, analysis requires about one-half hour.

Within recent years, a sensitive ultraviolet spectrophotometric method has been developed. This method, first introduced by Murray (36) for the analysis of phenolic compounds in gasoline fractions, makes use of the bathochromic shift in the spectrum due to the formation of the phenolate ion in alkaline solutions. This method has been used for a variety of phenolic compounds in many different applications, is the most sensitive procedure developed, and does not suffer from many of the problems associated with the other methods. The procedure requires less than 5 minutes for an analysis and is not affected by the structural characteristics of the substituted phenols. Other workers have refined the procedure, and indications are that, in addition to greater sensitivity and freedom from interference, the method is capable of detecting phenols in much a lower concentration range than other procedures can (16, 37-44). The method obviously overcomes the difficult problems encountered in the analysis of water and wastewater containing a variety of phenolic compounds in varying concentrations. The procedure has led to the development of instrumentation for the specific analysis of phenolic compounds in water and wastewater. The objective of this project was to evaluate this commercial instrument.

CONCLUSIONS

A careful review of the literature shows clearly the limitations and problems that have evolved in the development of analytical methods for the determination of phenol in water and wastewater. All of the proposed methods depend on a reaction with the aromatic ring of phenol. This fact places limitations on the analysis of a variety of substituted phenols, particularly ortho and para substituted phenols, since the O-H group directs reactions to these positions. In addition to this problem, the rate at which various test reagents react with the phenol ring varies considerably. The ultraviolet spectral method on which this work is

based is dependent on the ability of the phenol O-H group to ionize. This ionization, which occurs as the pH is shifted from acidic to basic conditions, allows for correlation of the concentration and ion formation of phenol. The bathochromic shift which occurs as the acidity and basicity are changed permits a reliable measure of phenol concentration. Thus, this method is dependent on the presence of the phenolic O-H group and independent of the positional substituents present. However, it is recognized that the type of substituents can affect the absorptivity and the bathochromic shift of some phenolic compounds, but the effect is minimal in most instances.

The PH-2 instrument evaluated provided several advantages over the 4-AAP method presently accepted as the standard procedure. The PH-2 procedure requires, as the only reagents, one drop of concentrated acid and two drops of saturated solution of alkali. In the actual measurements, one drop of concentrated phosphoric acid was sufficient to bring the phenol solutions to a pH of 4.0, and two drops of saturated solution of sodium hydroxide shifted the pH to a value of 12. The procedure allows for a rapid analysis since it involves setting the meter at zero with the solution at pH 4 and then reading the meter directly when base is added to the solution to bring the pH to a value of 12. It was found that the pH was not critical and that approximate minimum pH values sufficed. A single measurement can be made in less than three minutes, exclusive of any distillation that may be necessary. However, more care and time are needed if the expanded scale for ppb concentrations is used, because of the extreme sensitivity of the dial in establishing the zero reading. Nonetheless, no more than five minutes are needed, including dilution of samples, for the determination and calculation of the results obtained. It should also be noted that no more than a 50-ml sample is needed for a single analysis, about 10-ml for use with the 2-cm cell or about 35-ml for the 10-cm cell.

As indicated by the experimental data, this procedure has the significant advantage over the 4-AAP method in that it will detect para substituted phenols. It should be noted that this ultraviolet spectral method gives values which are higher than those derived from the 4-AAP methods. This fact is also noted in the analysis of the industrial samples. These higher values probably are due to the fact that, in some instances, the color formation reaction with the 4-AAP is incomplete which gives lower values in this method while in the ultraviolet spectral method, the conversion of the enol (phenol) to the phenolate ion is essentially complete and independent of the substituents. Thus, this commercial instrument is capable of providing a more complete assessment of the concentration..

The disadvantage of the ultraviolet method is the problem of detecting phenols which can exist as tautomers. The experimental data show that these compounds lie outside the absorption maxima for phenol and the phenolate ion. The existence of these substituted phenols as tautomers is well documented in the literature and their observed spectral behavior is not unexpected. However, an appropriate procedure for the determination of these substances should be established.

A representative and appropriate number of real (industrial) samples were also analyzed. It is significant that a wide range of concentrations are represented and that, in general, the analyses are higher than with the 4-AAP method. Although for some samples, 4-AAP analyses were determined by the laboratories, the results were not available for this work. These industrial samples represented a wide variety of sources, including both rural and urban water treatment plants, industrial plants, and foundries. All of the samples were preserved with copper sulfate and phosphoric acid, and it was necessary to distill each one prior to the analysis.

The error analysis of the data obtained from the several runs provides an indication of the accuracy and precision of the instrumental procedure. The accuracy was determined by a measure of the observed and true values for a series of solutions using the 2-cm cell and the 10-cm cell. The results show a range of 1.5-7.0% accuracy for the 2-cm cell and 10-25% for the 10-cm cell.

An important consequence of this work was that it provided an excellent opportunity for the students who assisted in the project to apply their theoretical training and knowledge to a very practical problem. It provided the students with an opportunity to extend their training in a productive and challenging manner. Thus, for those associated with the project, the problem served a twofold purpose--the challenge of completing a practical problem as well as applying theoretical training to a commercial problem.

RECOMMENDATIONS

The instrument provides for the measurement of phenolic compounds in the range of 50 ppb to 50 ppm. An expanded scale, which increases the sensitivity of the instrument, is provided for use in the low parts per billion range. Because of the increased sensitivity when used with the expanded scale, the instrument requires more care (almost complete damping) in setting the zero point. Although the additional care and time involved is not excessive, it is recommended that a vernier dial be incorporated in the instrument for use with the expanded scale. This will permit a more precise setting of the zero point with a less sensitive dial, and thus conserve time.

The quantitative measurement of phenolic compounds in water and wastewater by the PH-2 instrument is based on the bathochromic shift that occurs in phenol when the pH of the solution is shifted from acidic (pH 4.0) to basic (pH 12.0) conditions. The instrument, which uses hollow cathode lamps as its light source, is designed to measure phenolic substances as phenol. However, it is obvious that all phenolic substances do not have the same absorption maxima as phenol. This work shows that certain substituted phenols give values which are considerably less than the theoretical values. This has been ascribed to the fact that these phenolic substances have absorption maxima which lie outside the range of the instrument. It is recommended that consideration be given to

adding another lamp to measure the bathochromic shift of the phenolic substances which are incompletely detected. In particular, this lamp should be designed for the measurement of the chlorinated phenols which are serious pollutants and which appear to be positively, but incompletely, detected by the PH-2 instrument. The lamp should be installed so that it may be conveniently moved in and out of the measurement path.

The experimental data show that those substituted phenols which are capable of existing as a tautomeric equilibrium mixture are not detected by the PH-2 instrument. This may be due to the fact that the bathochromic shift of these compounds lies outside the absorption maxima of phenol and/or that, in a basic solution, the keto form is favored and thus gives anomalous spectral results. It is recommended that users of the instrument be made aware of the anomalous results to be expected from substituted phenols that can show tautomeric behavior.

Although the Ministil (MS-1) was used in this work, no recommendation is made for its use with the PH-2 instrument. This unit was designed as an adjunct to the PH-2 instrument for the unattended distillation of precisely 50-ml samples. This still is a very useful device but its present cost prohibits any recommendation for its use instead of the standard distillation equipment. Further consideration should be given to the application of this unit before a recommendation is made.

OBJECTIVES

Most of the methods investigated for the analysis of phenolic compounds in water have been found to have some deficiencies which limit their application. The spectrophotometric method shows the greatest promise because of its reliability, ease and rapidity of measurement, and possible adaptability to continuous monitoring. Based on the knowledge of the limitations encountered in other methods, a commercial spectrophotometer has been developed and is now available for the determination of phenolic compounds in water. The instrumental technique takes advantage of the bathochromic shift in phenolic compounds, which allows for a quantitative measure of phenolic substance.

Thus, the major objective of this project was to evaluate the utility of the recently available commercial instrument designed specifically for the determination of phenolic compounds in water and to study the instrumental and experimental parameters so that any improvements in sensitivity and reliability of analysis of phenols can be realized. An added objective was to provide the resources, capability, and support of the Department of Chemistry, Central State University, to the solution of a problem confronting the management of water quality.

INSTRUMENT DESIGN

The instrument investigated is an ultraviolet ratio spectrometer manufactured by Spectro Products, Inc., New Haven, Connecticut, and which has the trade name, PH-2. It consists of two conventional hollow cathode lamps which, by means of a square-wave amplifier, are pulsed 180 degrees out of phase, a monochromator, and a photomultiplier tube. The hollow cathode lamps are chosen so that light from one lamp is absorbed by the solution under acidic conditions while the other lamp is insensitive under these conditions. When the solution is made basic, light from the one lamp is absorbed and the other lamp is insensitive. The difference in the absorption under the acidic and basic conditions is proportional to the concentration of phenolic compound present. Because the instrument does not differentiate between various types of phenolic compounds, the results are reported as phenol. Fortunately, the extent of the bathochromic shift of phenolic compounds is independent of the concentration of the base; therefore, a pH of approximately 12 is sufficient to effect the shift and permit a quantitative measure of the phenolate ion.

During the evaluation, problems were encountered because the meter needle drifted inordinately during a given reading. This problem was corrected when the manufacturer improved the electronic circuit of the instrument, and no drift has been noted over an eight-hour period. The noise in the instrument can be decreased by use of the damping control without any significant loss in accuracy. The instrument is capable of increasing the sensitivity of low readings by converting the full scale to 0-10%, but more care and attention must be given to balancing the lamps. Thus, more time is required if one operates at the higher sensitivity setting, but the time required for an analysis can still be less than five minutes.

This method requires as reagents only an acid and a base. After any necessary distillation, the sample is adjusted by a drop of concentrated H_3PO_4 to pH 4. The solution is placed in the absorption cell and the proper lamp is adjusted to read zero. The cell is removed and the solution is adjusted to pH 12 by the addition of a base. It has been found that two drops of saturated sodium hydroxide are sufficient to bring the solution to a pH of 12. The cell and contents are returned to the spectrometer and the reading is observed. As a precautionary measure, it is important that the cells be washed thoroughly after each reading to avoid any cross contamination. The concentration of phenol may be determined directly from a standard curve which may be prepared, or by calculation from the equation:

$$\text{Phenol, ppm} = K \log \frac{\text{100-meter reading}}{100}$$

where K is the calibration constant. The equation is a form of the Beer-Lambert law as related to the specifics of the instrument and of phenol.

APPARATUS AND REAGENTS

Reagent grade chemicals were used throughout this study, and they were purchased from a single source.

All solutions were prepared using phenol-free water. The phenol-free water was prepared by passing distilled water through a glass column packed with a 4-cm X 25-cm column of 8-10 mesh activated animal charcoal. The phenol-free water was checked periodically, and the column was repacked whenever the blank water showed a phenol content of over 5 ppb.

The prepared stock solutions of phenol and substituted phenols (0.5 g/500 ml) were stored in a refrigerator. Fresh stock solutions were prepared after two weeks, if the stock solution had not been depleted. All other solutions were prepared fresh on the day of use by the appropriate dilution of the stock solutions.

The solutions of ammonium chloride, 4-AAP, and potassium ferricyanide for the color reaction in the 4-AAP method were prepared fresh each day in accordance with the procedures described in American Society for Testing and Materials (ASTM) and American Public Health Association (APHA) manuals (27, 28) for the direct photometric procedure and the chloroform extraction procedure.

All pH measurements were made with a Sargent-Welch Model PBL pH meter equipped with a combination electrode and standardized with a commercial pH 10 buffer.

All colorimetric measurements made by the 4-AAP method were made with a Bausch and Lomb Model 70 spectrophotometer. Initially, the response of the instrument was checked by preparing a Beer's law plot of standard sodium dichromate solution. The PH-2 instrument was used in accordance with the manufacturer's instructions.

All glassware used in the study was maintained in accordance with the procedure outlined in the quality control manual prepared by the Environmental Protection Agency (45).

The standard water distillation apparatus with ground glass joints was used. In addition, distillations were carried out with Ministils (MS-1) manufactured by Spectro Products, Inc.; these units provided for the unattended distillation of 50-ml samples and were designed for use with the PH-2 instrument.

The various industrial (real) samples obtained from several cooperating agencies were analyzed within 48 hours of the collection day and were kept refrigerated. All the industrial samples were preserved with copper sulfate and phosphoric acid in accordance with the recommended procedures (45) and were distilled prior to analysis.

EXPERIMENTAL

To evaluate this instrument objectively, the initial work involved obtaining a thorough study of and familiarity with the 4-AAP method and with the operation of the PH-2 instrument. As recommended by the ASTM and APHA, the 4-AAP method involves two procedures--the chloroform extraction and direct photometry. The first procedure is used for samples containing less than 0.1 mg/l (100 ppb) of phenol and the latter for those containing more than 0.1 mg/l (100 ppb). The recommended upper limit for analysis by the direct photometric procedure is 5 mg/l, but appropriate dilution of samples may be made to remain within the recommended concentration range.

The initial work consisted of the application of both of the 4-AAP procedures to the analysis of synthetic samples of phenol and the preparation of a working curve for both procedures. In Table I, data are presented to show the results of the analysis of phenol solutions by the chloroform extraction and the direct photometric procedures. These results represent a large number of samples that were analyzed over an extended period of time by three different persons. To approximate real conditions, each analyst prepared his/her own solutions from a single stock solution and worked independently. In this manner, systematic errors in the techniques of the three analysts would average out. The wide range of the calculated standard deviation may be attributed largely to the variation in the rate of reaction of phenol with 4-AAP to form the colored product. As indicated previously, several reaction parameters, especially pH, time of color development, and temperature, appear to have significant effects on the analysis (31). It is significant that the smallest deviation occurs with those samples whose absorbance is in the 0.3-0.7 range (50-20%T). The variation in the amount of phenol found by analysis and in the standard deviation indicates the reliability of these two procedures. In agreement with the work of other investigators, the chloroform extraction procedure appears to be the more sensitive.

For routine determination of phenols in water, a working curve can be prepared and the concentration determined directly from it. This procedure is a time-saving device which can be used in laboratories where a large number of analyses are determined. However, the working curves must be checked periodically because of changes with time of the spectrophotometer. Using the data given in Table II working curves were prepared for the chloroform extraction and direct photometric procedures (Figures 1 and 2).

The evaluation of the PH-2 instrument was undertaken after a preliminary study was made of its operating parameters. Unlike the 4-AAP method, the PH-2 determination is not dependent on a color reaction but on the bathochromic discussed earlier. The method is thus independent of any substituents on the ring which have been shown to interfere in the analysis by the 4-AAP method. The only reagents needed are concentrated

Table I

Phenolic Concentration Values Determined by the 4-AAP Method

Number of measurements	Calculated conc.(µg/l)	Average conc. observed(µg/l)	Standard deviation
	Chloroform Extraction Procedure		
8	5	5.28	±0.94
16	10	9.82	±0.38
24	20	18.58	±1.10
26	30	30.47	±1.79
24	40	39.81	±0.52
16	50	49.89	±0.70
8	60	61.32	±1.03
8	70	72.67	±2.80
	Direct Photometric Procedure		
33	1.0 mg/l	0.95	±0.52
45	2.0	1.92	±0.85
36	3.0	2.84	±0.67
30	4.0	4.00	±0.45
36	5.0	5.05	±0.70

Table II

4-AAP Method - Preparation of Working Curve

Number of measurements	Calculated conc.(µg/l)	Average conc. observed(µg/l)	Standard deviation
	Chloroform Extraction Procedure		
4	10	9.97	±0.04
4	20	19.06	±1.06
4	30	28.92	±0.18
4	40	39.97	±0.22
4	50	49.95	±0.09
	Direct Photometric Procedure		
6	1.0 mg/l	1.01	±0.02
6	2.0	2.03	±0.08
6	3.0	3.00	±0.15
6	4.0	3.99	±0.11
6	5.0	5.10	±0.15

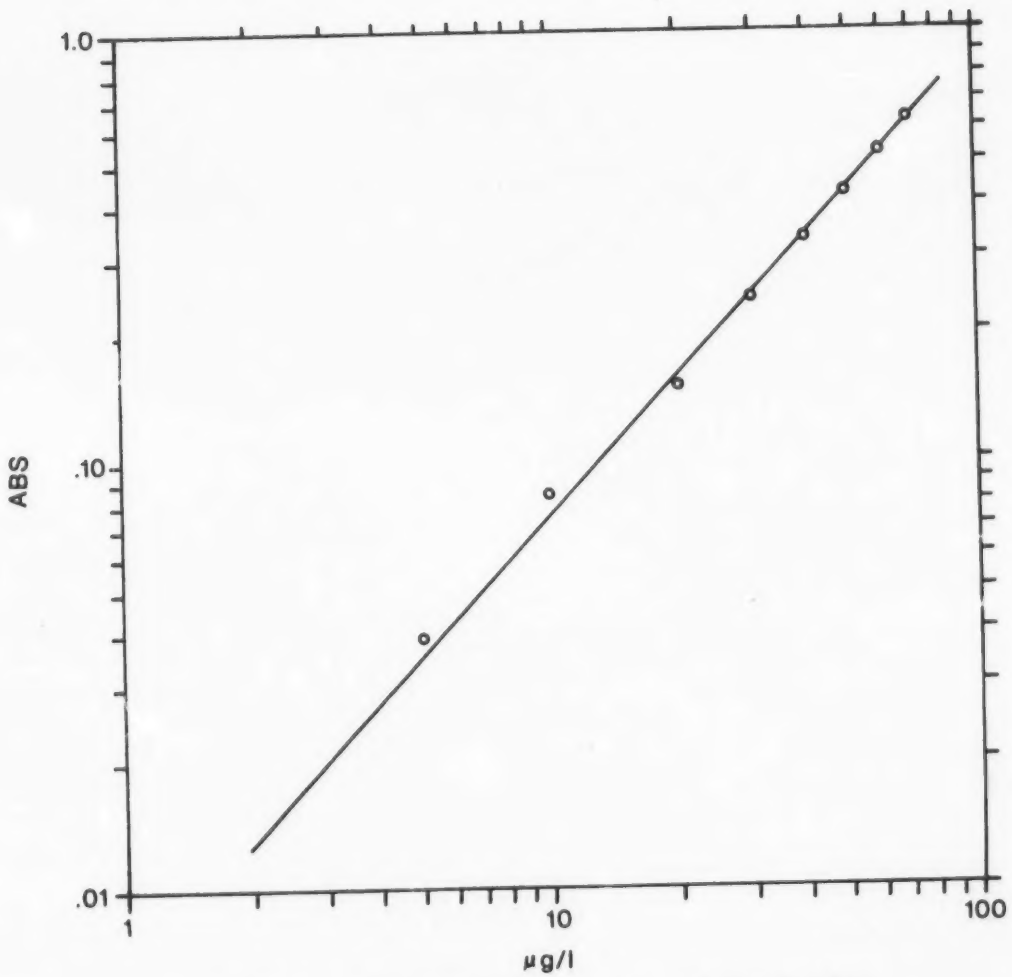


FIGURE 1. 4-AAP METHOD ($CHCl_3$ EXTRACTION)

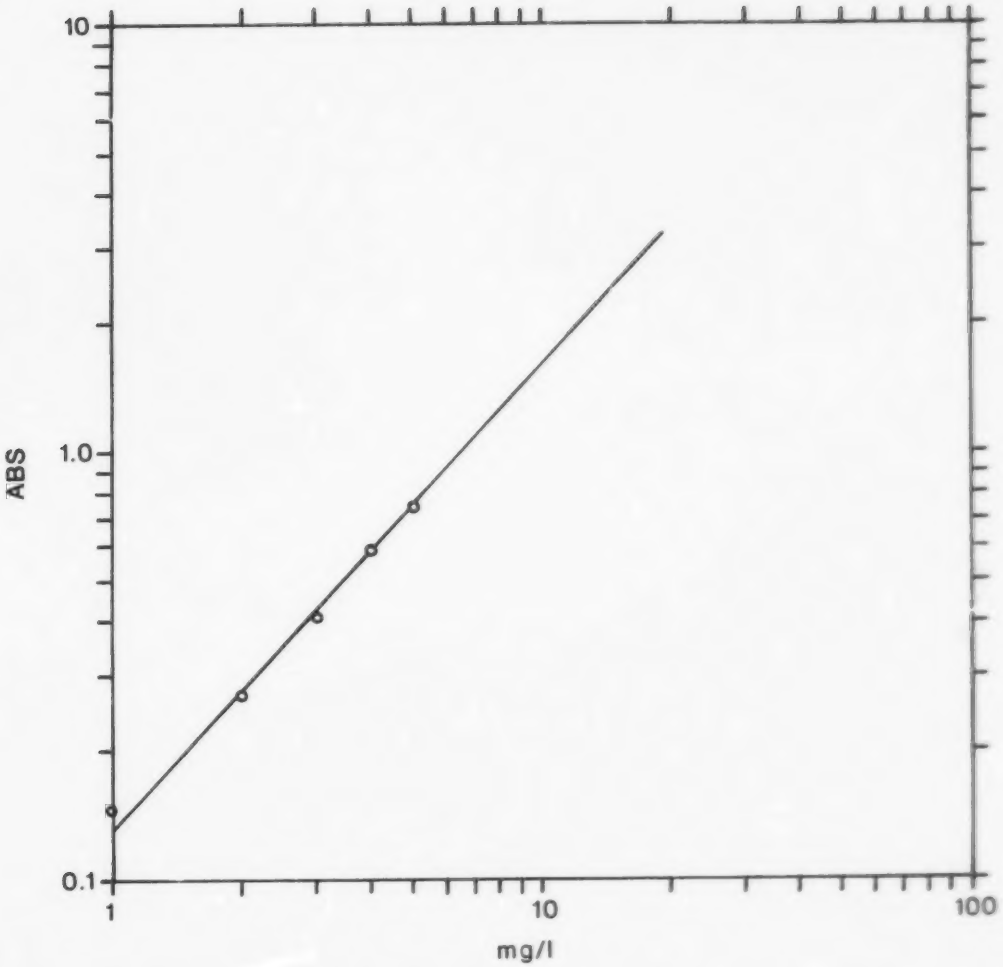


FIGURE 2. 4-AAP METHOD (DIRECT PHOTOMETRIC)

phosphoric acid and a saturated solution of sodium hydroxide. Studies have shown that the pH is not critical, as long as the acidity of the phenol solution is lowered to about pH 4.0 and the basicity is raised to about pH 12.0. The absorption cell containing the test solution is placed in the light path and the lamp adjusted to read zero. The cell is removed and sufficient base is added to bring the pH of the solution to about 12.0. The meter reading is applied to the following equation

$$\text{phenol (ppm)} = -K \log \frac{\text{100-meter reading}}{100}$$

K = calibration constant

to determine the concentration of phenol. Alternatively, a working curve can be prepared by plotting the meter reading against concentration, and the concentration of a sample determined from the curve. Two absorption cells are available; one cell has a path length of 2 cm for use in the 50 ppb to 50 ppm phenol concentration, and the other cell has a path length of 10 cm for use in the lower than 50 ppb concentration range. The instrument has provision for scale expansion for use with the 10-cm cell which is used in the lower concentration range. It was found that in all analyses, one drop of phosphoric acid was sufficient to shift the pH to 4.0, and two drops of saturated solution of sodium hydroxide were sufficient to shift the pH to 12.0.

The calibration constant had been determined for the instrument and reported to be 21.5. However, because of the necessary electronic modifications that had been made on this instrument by the manufacturer, the calibration constants were redetermined (Table III). The calculated value of 21.1 is in agreement with the value reported by the manufacturer for the 2-cm cell. The calculated value of the calibration constant of 4.32 for the 10-cm cell is in agreement with the reported value of 4.30. These calculated values were used in the calculation of the phenol concentration of the subsequent work reported herein. The calibration curves are shown in Figure 3.

Among the concerns of the evaluation of this instrumental method are the accuracy and precision in the measurement of phenols, the simplicity and rapidity of the measurements, and the ability to detect a wide range of phenolic compounds. It is these factors which limit the usefulness of the 4-AAP method, and which this instrument is designed to overcome.

A series of phenolic compounds was tested with the 4-AAP method and the PH-2 instrument (Table IV). Most of the compounds selected were para-substituted phenols, which are generally insensitive to the 4-AAP method. Among the phenols chosen are those with alkyl, halogen, amino, hydroxyl, nitro, and carbonyl substituents. The selection of these various types of substituents should provide a reasonable evaluation of the ability of the PH-2 instrument to respond to a wide variety of phenols. They include those which are more likely to be found as pollutants, since most have at least slight solubility in water.

Table III

Data for Determination of Calibration Constant, PH-2 Instrument

Phenol, conc. mg/l	K calibration constant	Average deviation
	2-cm cell	
2	21.23	±0.08
3	21.03	±0.18
4	21.38	±0.21
5	21.82	±0.37
10	20.21	±0.64
20	21.03	±0.24
	10-cm cell	
0.10	4.78	±0.21
0.02	4.36	±0.12
0.03	4.28	±0.11
0.05	4.10	±0.27
0.06	4.20	±0.09

As with other analytical methods for the detection of phenols, the PH-2 instrument is not capable of determining the concentration of specific phenols. The data obtained report the concentration of the various substances as phenol. However, it is expected that some variation may occur in the concentration of the substituted phenols because of the differences in the bathochromic shift experienced by the various phenols. Since the use of hollow cathode lamps gives monochromatic light of a very narrow wavelength, the maxima of absorbance of the phenols may fall outside the range of the lamps selected. Nonetheless, the results of this study show some significant features. Table IV shows the comparative data of the analysis of various substituted phenols with the 4-AAP method and with the PH-2 instrument. According to previous work, phenols substituted in the para position are insensitive to the 4-AAP method except those with halogen, carboxyl, hydroxyl, methoxy, or sulfonyl substituents since these groups are capable of being replaced in the oxidative reaction of 4-AAP with phenol. The data for p-hydroxybenzoic acid, p-chlorophenol, p-methoxyphenol, and 2,6-dichlorophenol support this observation. The results obtained for these phenols are low, but this may be due to several factors, such as time for development of color and incomplete displacement reaction in addition to the factor of shift of maxima mentioned above. However, as expected, the phenols having other substituents in the para position, such as p-cresol, 3,4-dimethylphenol, tyrosine, vanillin, p-aminophenol, p-tertbutylphenol and p-hydroxybenzaldehyde do not show any appreciable reaction with the 4-AAP method.

The response of the PH-2 instrument to these substituted phenols shows significant features. It will be noted that 4-nitrophenol shows no

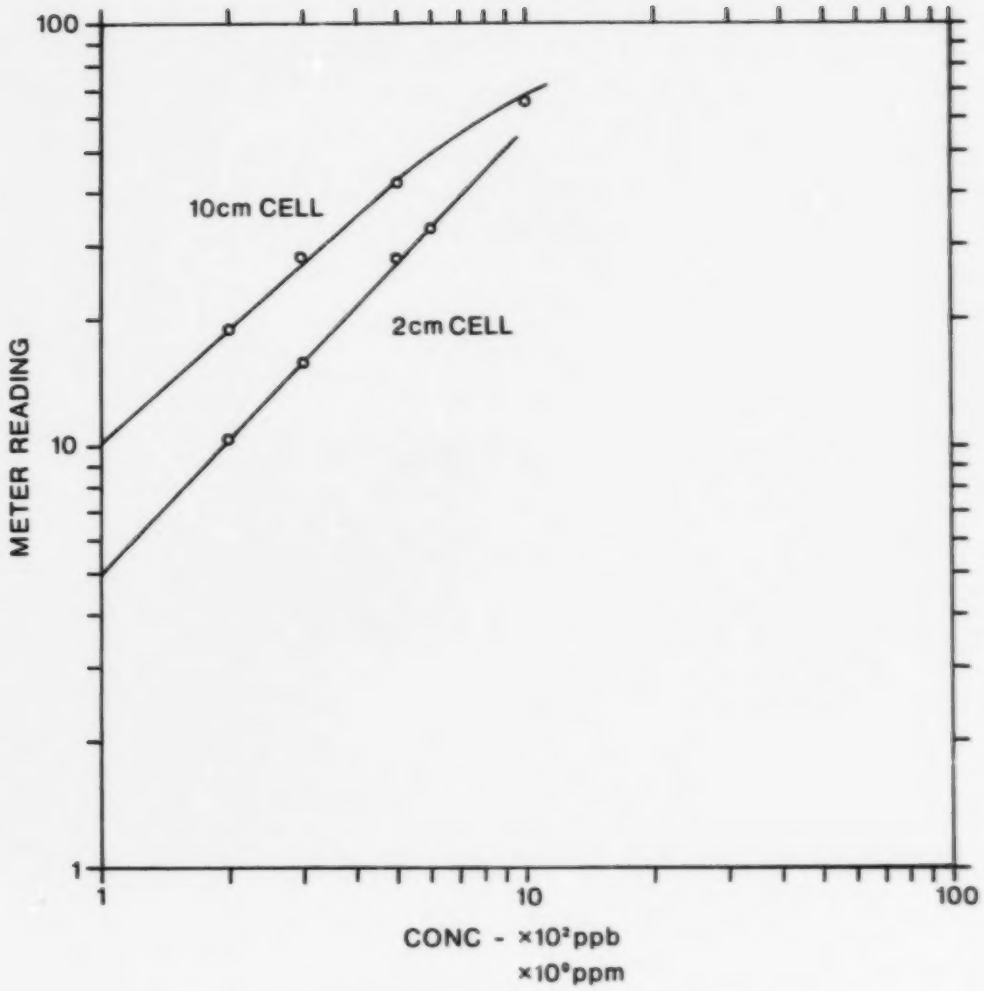


FIGURE 3. PH-2 INSTRUMENT

Table IV

Comparison of Methods with Substituted Phenols

Compound	Conc., calc. mg/l	Conc.,obs* 4-AAP mg/l	Conc.,obs* PH-2 mg/l
phenol	2.0	2.05 ± 0.04	2.06 ± 0.02
p-cresol	2.0	0.0	1.94 ± 0.05
m-cresol	2.0	1.77 ± 0.03	2.16 ± 0.03
2,6-dimethylphenol	2.0	0.94 ± 0.06	2.01 ± 0.03
3,4-dimethylphenol	2.0	0.14 ± 0.06	2.01 ± 0.08
4-nitrophenol	2.0	0.05 ± 0.14	****
l-tyrosine	2.0	0.27	1.99 ± 0.02
vanillin	2.0	0.03 ± 0.10	****
p-hydroxy benzoic acid	2.0	1.02 ± 0.08	2.02 ± 0.02
p-aminophenol**	2.0	0.05 ± 0.15	1.58 ± 0.08
p-chlorophenol	2.0	1.61 ± 0.25	1.19 ± 0.05
2,6-dichlorophenol	2.0	0.97 ± 0.09	2.00 ± 0.04
p-methoxyphenol	2.0	1.06 ± 0.12	****
p-tert-butylphenol	4.0	0.20 ± 0.03	3.03 ± 0.04
m-hydroxyacetophenone	2.0	0.60 ± 0.07	****
hydroquinone	2.0	0.22 ± 0.16	****
2,4-dichlorophenol	2.0	0.97 ± 0.11	0.25 ± 0.13
resorcinol	2.0	1.01 ± 0.1	2.38 ± 0.11
p-hydroxybenzaldehyde	2.0	0.0	****
2-naphthol	2.0	0.43 ± 0.15	1.75 ± 0.09
thiophenol	2.0	0.00	0.60 ± 0.12
4-methylthiophenol***	2.0	1.36 ± 0.08	0.61 ± 0.04

* Analysis run in triplicate; average deviation determined
** Practical grade; used without purification
*** Commercial grade
**** Instrument gave zero or negative reading for bathochromic shift

appreciable reaction with 4-AAP and no response with the PH-2 instrument. However, 4-nitrophenol is highly colored and this may lead to interferences. In addition, because of the color, the absorption maxima of the phenol and phenolate ion may be expected to lie outside the range of the instrument. It is significant that, with a few exceptions, those phenols which are unreactive in the 4-AAP method show positive results with the PH-2 instrument. The cresols and tyrosene and chlorinated phenols, which are the most important pollutants in this group, are detected by the PH-2 instrument.

It is significant that the compounds, vanillin, p-methoxyphenol, hydroquinone and p-hydroxybenzaldehyde gave no response with the PH-2 instrument. Similar problems were experienced with these substances with the 4-AAP method. However, a closer examination of these compounds shows that all contain a hydroxy or carbonyl substituent and, in general, represent phenol compounds which are capable of existing as tautomers. Considerable study has been done on the tautomeric equilibrium that may exist with the substituted phenols in acidic and basic media (46, 47). Since these specific substituted phenols can exist as a tautomeric equilibria, it is not surprising that they show an anomaly in their absorption spectra, and this factor suggests the reason they do not respond to the PH-2 instrument and behave as they do with the 4-AAP method. Thus, if these compounds exist as a keto-enol tautomeric equilibrium mixture, the maxima of the equilibrium mixture probably would not lie in the same absorption range as phenol. The absorption spectra of these compounds were run using the same concentration as shown in the data, and an examination of the spectra shown in the Appendix suggests that the anomalous behavior observed would be expected. In addition to the above specific compounds, resorcinol and naphthol show a large deviation from the calculated value, even though significant amounts of them were detected. However, it has been shown that these exist as a tautomeric equilibrium mixture, although the equilibrium greatly favors the enol form. It might be speculated that the significant deviation from the calculated value may be due also to the existence of such an equilibrium mixture in these compounds.

In addition to the comparison of the two methods on individual phenols, synthetic mixtures were prepared, and the results of the two methods were compared. The data for the synthetic mixtures are shown in Table V. The concentrations of the individual components in the mixtures were arbitrarily chosen, but the prepared mixture was selected for specific reasons and conditions. The mixture of phenol and cresols and mixture of cresols and chlorophenol were chosen because they frequently occur as pollutants. The other mixtures were prepared based on the results of the analysis of the individual compounds. Mixtures were prepared to contain compounds which were (1) insensitive to the 4-AAP method but detectable by the PH-2 instrument, (2) to contain compounds which were sensitive to the 4-AAP method but insensitive to the PH-2 instrument method, and (3) to contain compounds in which some were insensitive to one method but not to the other. The latter group of mixtures permitted the evaluation of both methods in detecting compounds in the presence of

extraneous compounds and to determine the influence on the analyses of these extraneous compounds. The results show good agreement with the calculated amount of phenols. It is uncertain if the analyses by the PH-2 instrument method are affected by the presence of phenols that can show the tautomeric effect. Additional work could be done to ascertain the effect of these tautomeric phenols, but at present, they do not represent serious pollutants and have not been reported as pollutants in water, even though they are water soluble. The average deviation was determined rather than standard deviation, because the samples were run in triplicate only and sufficient number of analyses were not made to warrant a greater statistical analysis.

The accuracy of the PH-2 instrument was determined by preparing known samples of phenol and adding known amounts of phenol ("spikes"). This procedure provides a means of determining the amount of recovery of phenol when added to another sample. The samples prepared included the range of concentration of parts per million to parts per billion of phenol. The range of concentrations used represent the range of detection of phenol by the PH-2 instrument, including the expanded scale. The experimental work involved initially the preparation and analysis of phenols of known and varying concentrations. An aliquot was removed from the initial sample and an aliquot of a known concentration of phenol was added and the sample again analyzed. An appropriate correction was made for the amount of sample withdrawn and the amount added. In each instance, the aliquot removed was equivalent to the amount added so that the initial and final volumes remained constant. Correction was made for the amount of phenol removed. All of these experiments were performed on phenol solutions and several samples were "spiked" with p-cresol instead of phenol. Also included in this study was the addition of "spikes" to several industrial water samples that were collected and analyzed. The data for these studies are shown in Table VI. For these experiments, no comparable studies were conducted with the use of the 4-AAP method, since the purpose of the study was to determine the accuracy and reliability of the PH-2 instrument. The samples were run in triplicate and only the average deviation was determined. The data show a high percent recovery of phenol which in turn indicates the accuracy of the instrument in determining phenol over a wide range of concentrations.

In Table VII are shown data on the analysis of a variety of industrial wastewater samples. All of the samples were collected and preserved with copper sulfate and phosphoric acid by the agencies from whom the samples were obtained. The samples were analyzed within a 48-hour period after collection. All of the samples were kept refrigerated until the analyses were completed. The samples were collected monthly over a six-month period, and thus represent a reasonable spectra of environmental conditions. The sampling sites included a rural and municipal water treatment plant, a foundry, a chemical manufacturing plant, an agricultural stream, and downstream river sites. The variety of the sampling sites provided a possible wide range of phenol concentrations in water. The samples were analyzed by the 4-AAP method and by the PH-2 instrument method. In some instances, the sample size was not sufficient to run triplicate samples

Table V

Comparison of Results Obtained for Phenols in Distilled Water by the 4-AAP and PH-2 Methods

	Mixture	Conc. (mg/l)	Total conc. mg/l (calc)	Total conc. mg/l (obs) 4-AAP	Total conc. mg/l (obs) PH-2
I.	phenol	5.0			
	p-cresol	2.0			
	m-cresol	1.0	8.0	5.8	8.0
II.	p-cresol	5.0			
	m-cresol	5.0			
	p-chlorophenol	1.0	11.0	4.9	9.3
III.	phenol	4.0			
	p-methoxyphenol	2.0			
	p-cresol	2.0	8.0	5.7	5.0
IV.	p-cresol	3.0			
	3,4 dimethylphenol	3.0			
	p-tert-butylphenol	3.0	9.0	6.7	9.30
V.	p-chlorophenol	4.0			
	resorcinol	2.0			
	m-cresol	2.0	8.0	5.66	8.21
VI.	p-cresol	4.0			
	4-tert-butylphenol	2.0			
	3,4 dimethylphenol	2.0	8.0	3.6	8.03
VII.	p-methoxyphenol	3.0			
	hydroquinone	3.0			
	m-hydroxy acetophenone	3.0	9.0	2.97	no response
VIII.	tyrosine	2.0			
	p-hydroxyzoic acid	2.0			
	p-tert-butylphenol	2.0	6.0	1.4	5.18

Table VI

Recovery of Phenol by the PH-2 Instrument Method

Sample	Phenol in sample mg/l	Phenol added mg/l	Phenol found mg/l	% Recovery
1	2.14	.08	2.87	97
2	0.98	1.80	3.20	111
3	2.03	2.40	4.77	108
4	4.17	0.60	4.73	99
5	3.07	0.90	4.00	100
6	0.33	0.04	0.36	97
7	0.03	0.04	.06	86
8	0.02	.02	.03	75
9	0.04	0.10	0.12	86

for both analytical procedures. The values reported are average values. With few exceptions, the PH-2 instrument data showed consistently higher results than the 4-AAP method. This result is not unexpected since the previous work has demonstrated clearly that the PH-2 instrument will detect phenols which are insensitive to the 4-AAP method of analysis. This fact would suggest that these water samples contained substituted phenols which would escape detection by the 4-AAP method. No reasonable explanation can be given for those results in which the 4-AAP analyses were higher than with the PH-2 instrument, unless it can be assumed that these samples contained phenols or other substances which enhanced the 4-AAP color reaction and thus gave anomalous results. It is not reasonable to expect that these samples contained substituted phenols which would give anomalous results with the PH-2 instrument as shown above with the substituted phenols which can exhibit tautomerism.

DISCUSSION

The initial work of this project included a thorough review of the literature of the various methods available for the analysis of phenols in water and wastewater. An evaluation of these methods indicates that the 4-AAP method is the most reliable and less time-consuming of the various colorimetric methods. On the other hand, it is obvious that it has several serious limitations, primarily its dependence on reacting a reagent with the aromatic ring of phenol to produce a colored product which is measured and related to the concentration of phenol. The ultraviolet spectral method appears to overcome many of the limitations of these other methods. It is dependent on the shift in absorption maxima (bathochromic shift) as the phenol in acid solution is converted to the phenolate ion in a basic medium. Thus, it is independent of the substituents on the aromatic ring of phenol and does not rely on any reaction of the ring.

Table VII

Phenol Concentration of Industrial Samples
(Average Values)

Sample	Concentration µg/l 4-AAP	PH-2
120	36.9	48.6
121	11.9	19.7
122	51.6	25.7
123	45.2	47.9
124	45.2	47.0
125	39.3	40.5
126	4.8	31.0
127	83.3	93.8
128	15.5	19.6
129	44.1	46.8
130	10.7	10.8
131	93.0	14.3
132	128.0	196.0
133	40.0	94.0
134	24.0	94.0
135	39.0	230.0
136	142.0	380.0
137	65.0	141.0
138	192.0	240.0
139	40.0	94.0
140	48.0	85.0
141	35.7	58.0
142	0.0	14.0
143	7.7	49.0
144	17.9	88.0
145	836.0	832.0
146	160.0	230.0
147	0.0	18.0
148	403.0	954.0
149	1480.0	3460.0

The experimental work encompassed evaluating the PH-2 and comparing it with the 4-AAP method. The initial work included the preparation and analysis by the 4-AAP method of synthetic samples of phenol varying in concentration from 0.01 to 5 mg/l. The initial experimental work provided a thorough familiarity with the 4-AAP method. Similar kinds of experiments were conducted with the PH-2 instrument to gain a familiarity with its operation and response. Significantly, the PH-2 gave more reproducible and more precise results than the 4-AAP method. This work on the comparison of the two methods was extended to a large variety of substituted phenols. The substituted phenols were selected to represent the most frequently occurring phenols, those which have been reported as pollutants, and those that have substituents in the ortho-, meta-, and para-positions of the aromatic ring. This work clearly demonstrated the limitation of the 4-AAP method in determining phenolic compounds with certain substituents in the para-position. The same phenols which are not detected by the 4-AAP method are detected by the PH-2 instrument.

However, it is significant that some substituted phenols are not detectable by the PH-2 instrument. It was found that hydroxyl or carbonyl substituted phenols give anomalous results. Also, it was found that some of these specific phenols were not detected by the 4-AAP method. A close examination of the structure of these phenols show that they are capable of existing as a tautomeric mixture, which may explain their anomalous behavior. An examination of the literature showed that in solution, the tautomeric equilibrium mixture of these phenols favors the keto form. Fortunately, most of these particular phenols have not been reported as serious water pollutants. The ultraviolet spectra of these phenols were studied, and it was found that their absorption maxima lie outside the range of the instrument and outside the wavelength used in the 4-AAP method. However, no attempt was made to develop a technique for their measurement under the present experimental conditions, but if it should become necessary to measure these phenols, a comprehensive study must be undertaken.

Experimental work was carried out to determine the accuracy of the PH-2 instrument by adding phenol of a given concentration to a known and measured concentration of phenol. The amount of recovery was then determined, and it was found that the instrument provided accurate analyses. Again, varying concentrations of phenol were used which covered the range of the instrument. A few experiments were conducted which included the addition of a given concentration of a substituted phenol to known concentrations of phenol. These experiments, along with the previous work demonstrated the reproducibility and reliability of the instrumental method of analysis of phenol.

An error analysis was made of the data obtained from the PH-2 instrument to ascertain the accuracy of the measurements. These data were obtained as the difference between the observed and true values divided by the true value with the result presented in percent. In Table VI are shown data for measurements of spiked samples with the use of the 2 cm

and the 10 cm cells designed for measurement in the 50 ppb-50ppm and 5 ppb-50 ppb range, respectively. Analysis of the data shows a 1.57% accuracy for the 50 ppb-50 ppm range and 10-25% accuracy for the 5-50 ppb range. The average value of the accuracy for the 50 ppb-50 ppm range is ±4.7%, and the average value for the 5-50 ppb range is ±11.9%. These values indicate that the range of accuracy for the PH-2 instrument is acceptable.

Although it was necessary to conduct experiments with known concentrations of phenol and substituted phenols, it was also necessary to test the instrument with real samples. Through the cooperation of a local agency, industrial samples were made available. They were analyzed simultaneously by the 4-AAP method and the PH-2 instrument method. In nearly all instances, the PH-2 instrument gave higher results for the phenol content. This may be explained in either of two ways: (1) substances were present which interfered and lowered the values obtained by the 4-AAP method; or (2) the PH-2 instrument was capable of determining phenols in the samples that were not detected by the 4-AAP method. A few samples did show higher results with the 4-AAP method and this may be due to interfering substances that enhanced the color developed by the 4-AAP method, or interfered with PH-2 instrument readings. A more comprehensive study would be needed to identify clearly the reasons for the results. However, it can be established that the PH-2 instrument is capable of adequately analyzing wastewater samples.

This work was limited to the evaluation of the PH-2 instrument and no attempt was made to assess the cost projections for the instrument. However, it should be mentioned that the instrument employs hollow cathode lamps which are identical to those used in atomic absorption units, and experience has shown that they have a life of about two years. Other maintenance costs should be comparable to any other ultraviolet spectrophotometer. The only reagents required are concentrated acid and saturated solution of alkali. For each analysis, one drop of concentrated phosphoric acid and two drops of saturated sodium hydroxide solution are sufficient. Thus, the cost of reagents is much less than in other methods.

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APPENDIX D

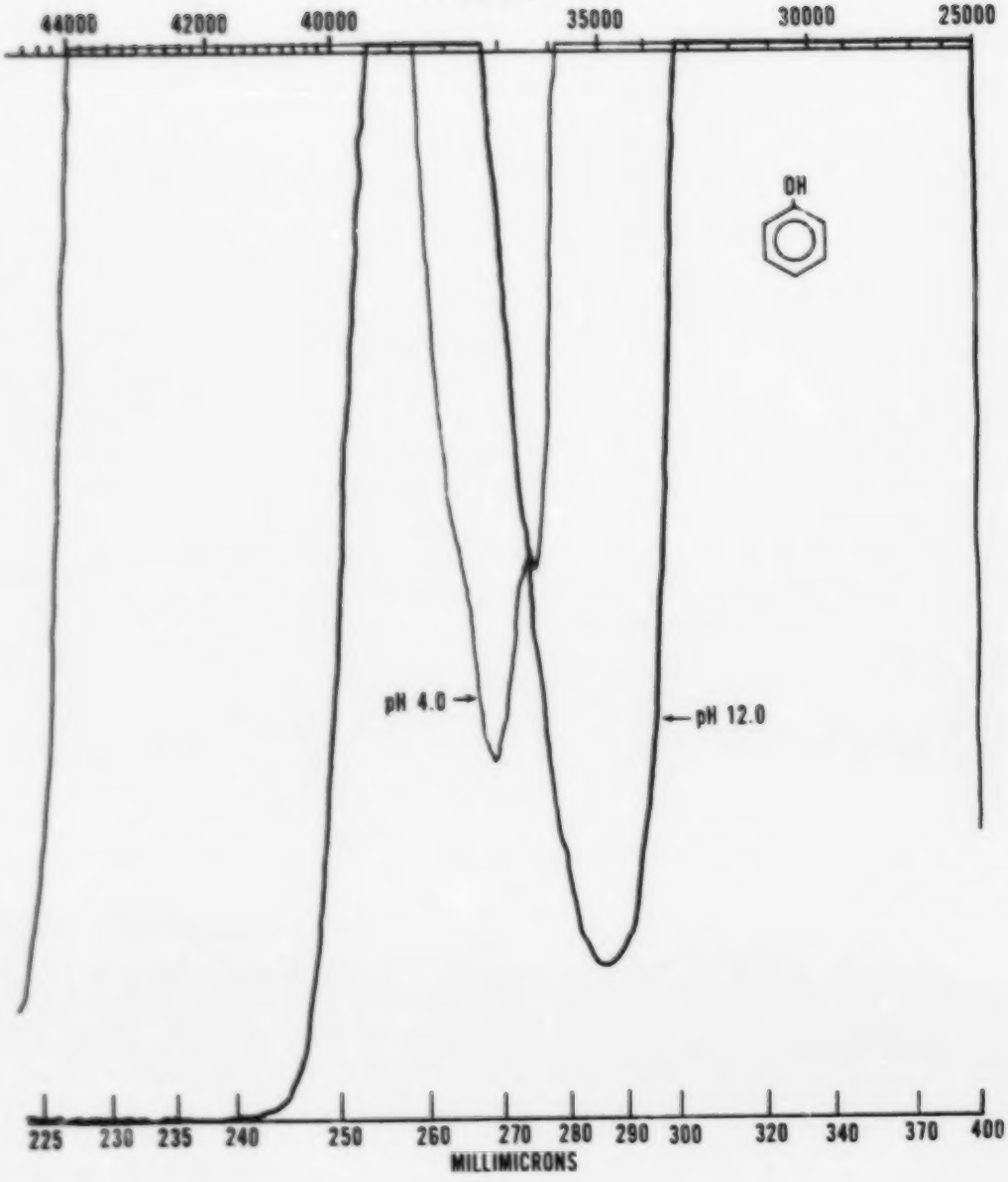

FIGURE 1. PHENOL

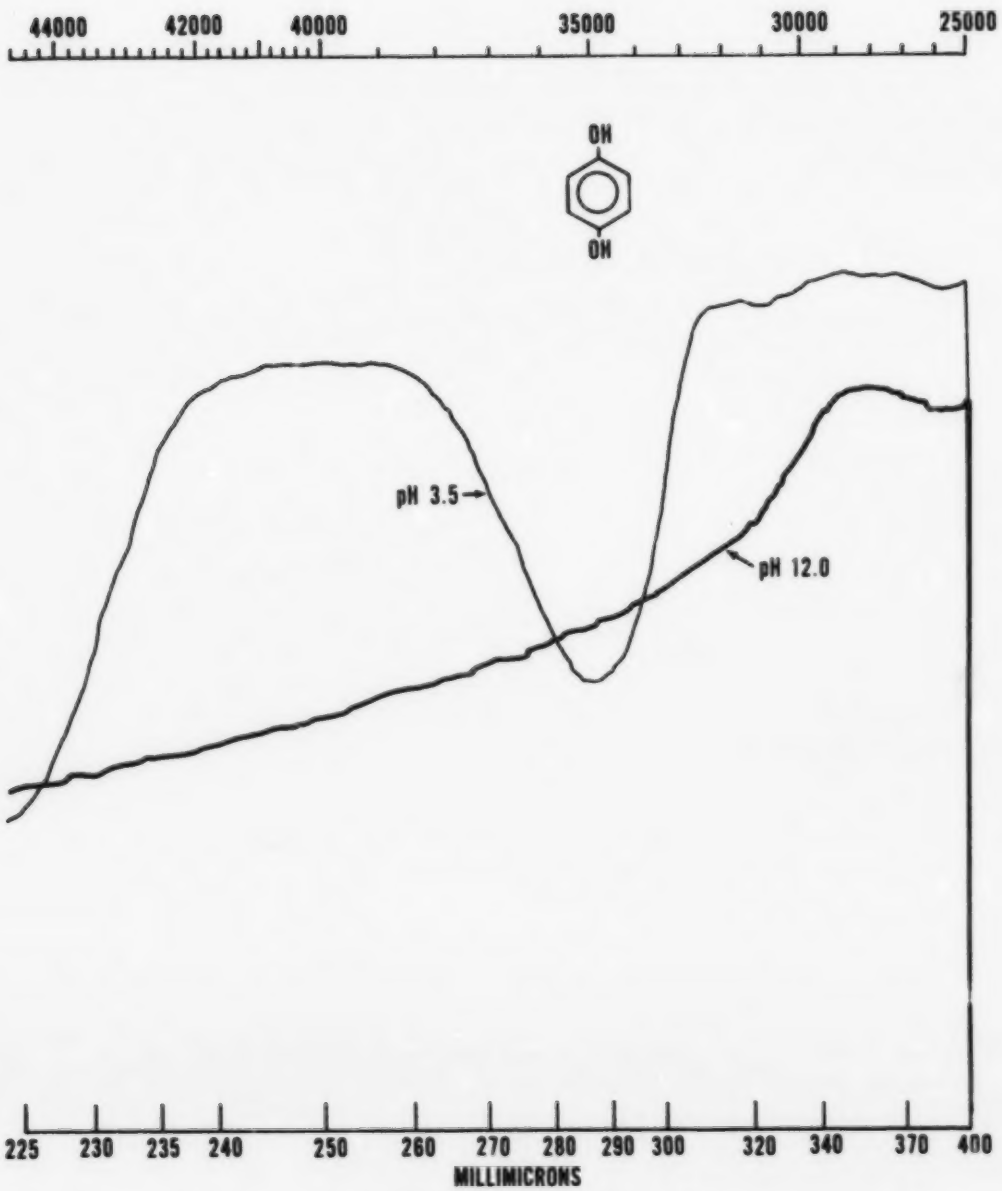

FIGURE 2. HYDROQUINONE

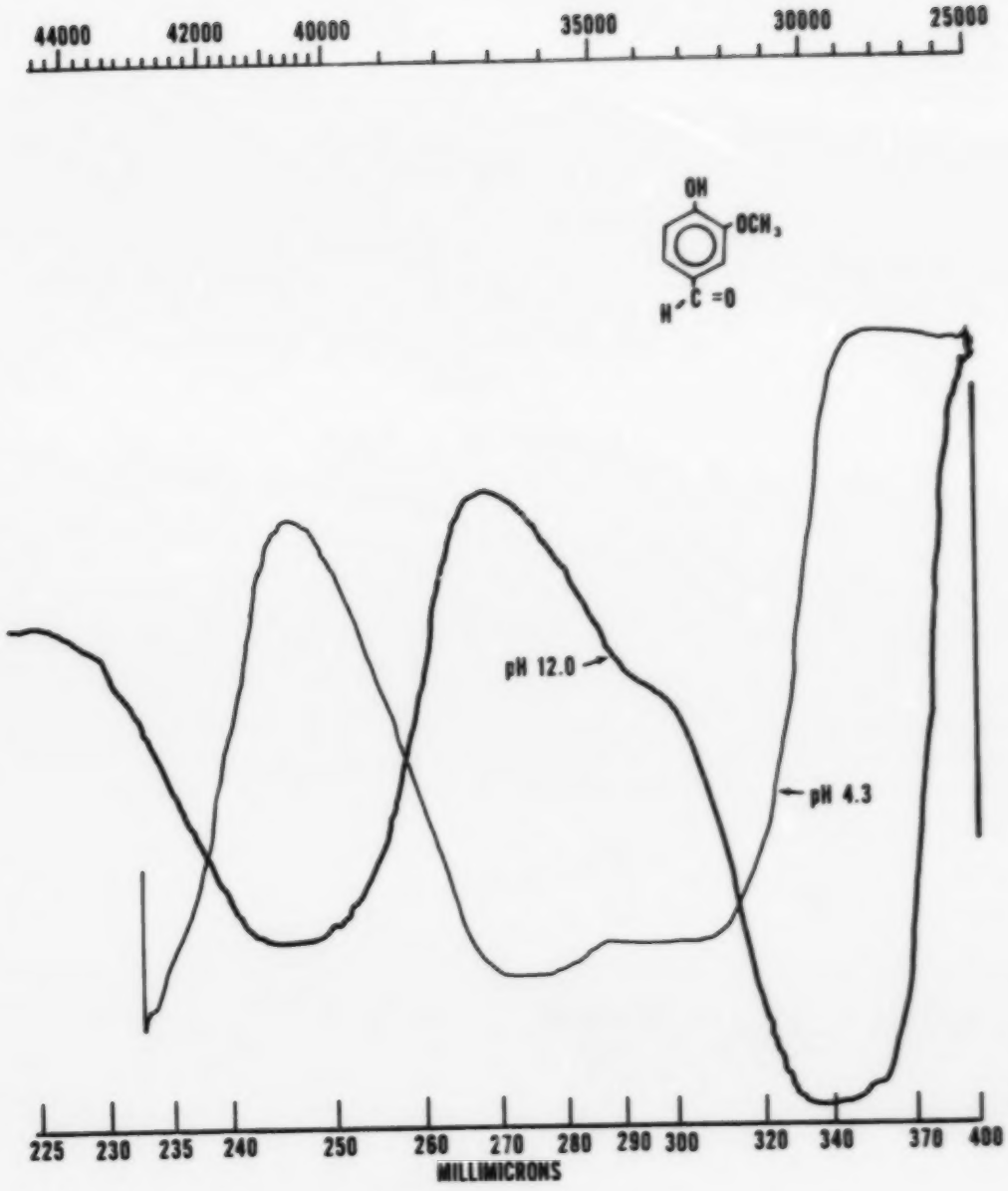

FIGURE 3. VANILLIN

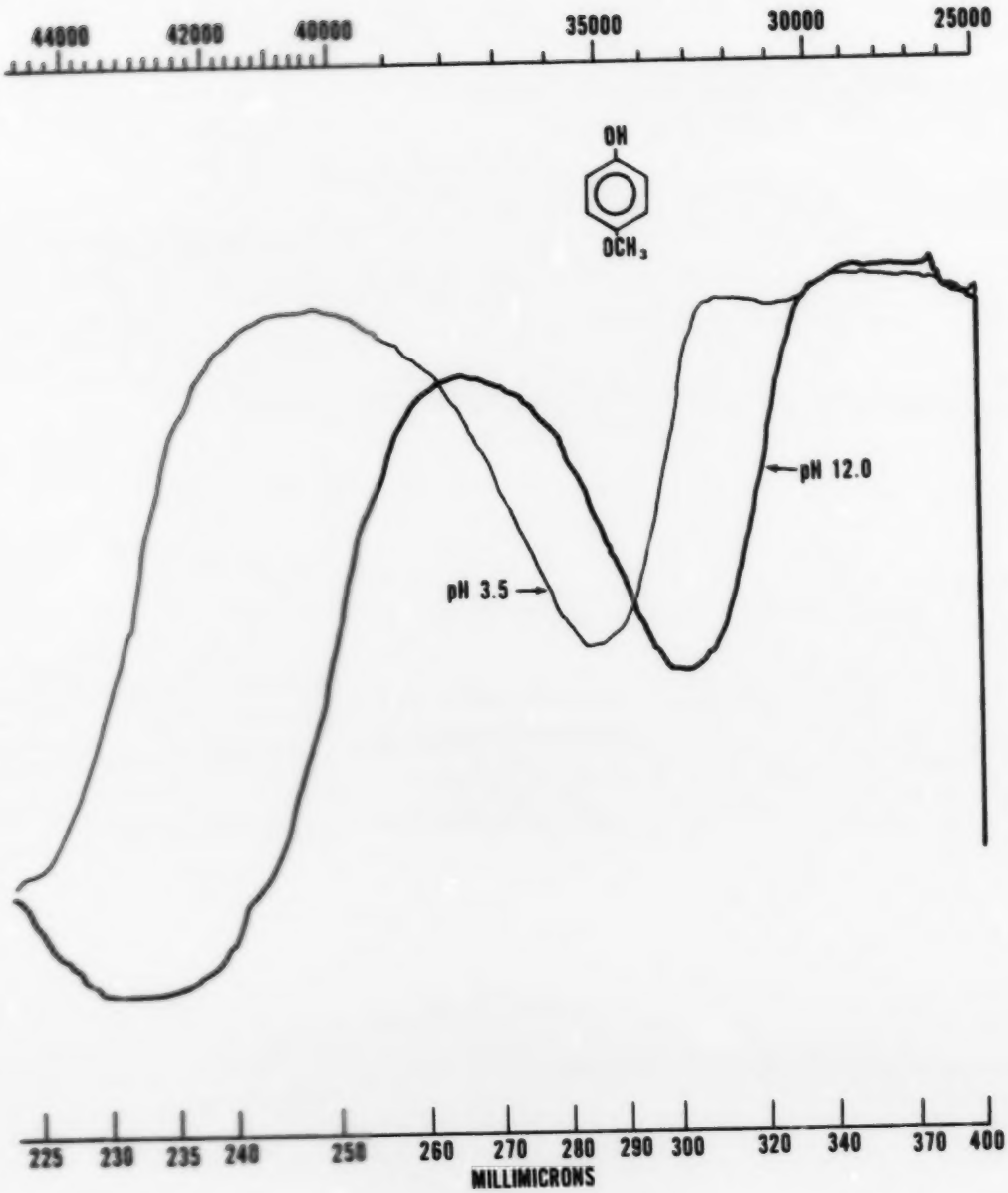

FIGURE 4. 4-METHOXYPHENOL

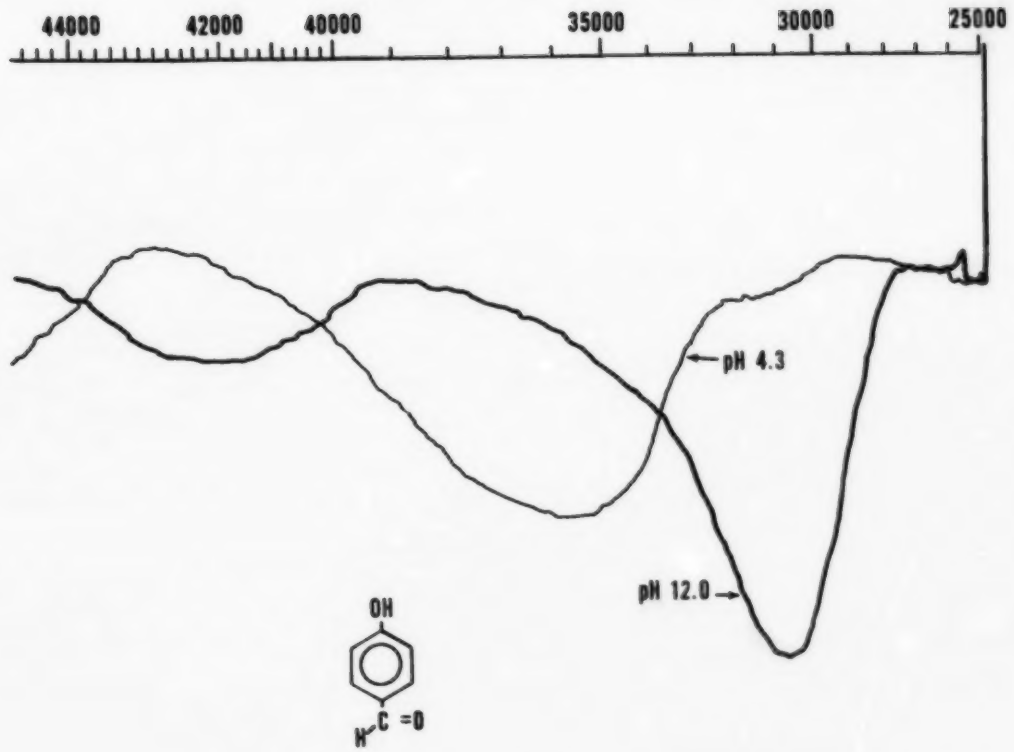

FIGURE 5 . 4-HYDROXYBENZALDEHYDE

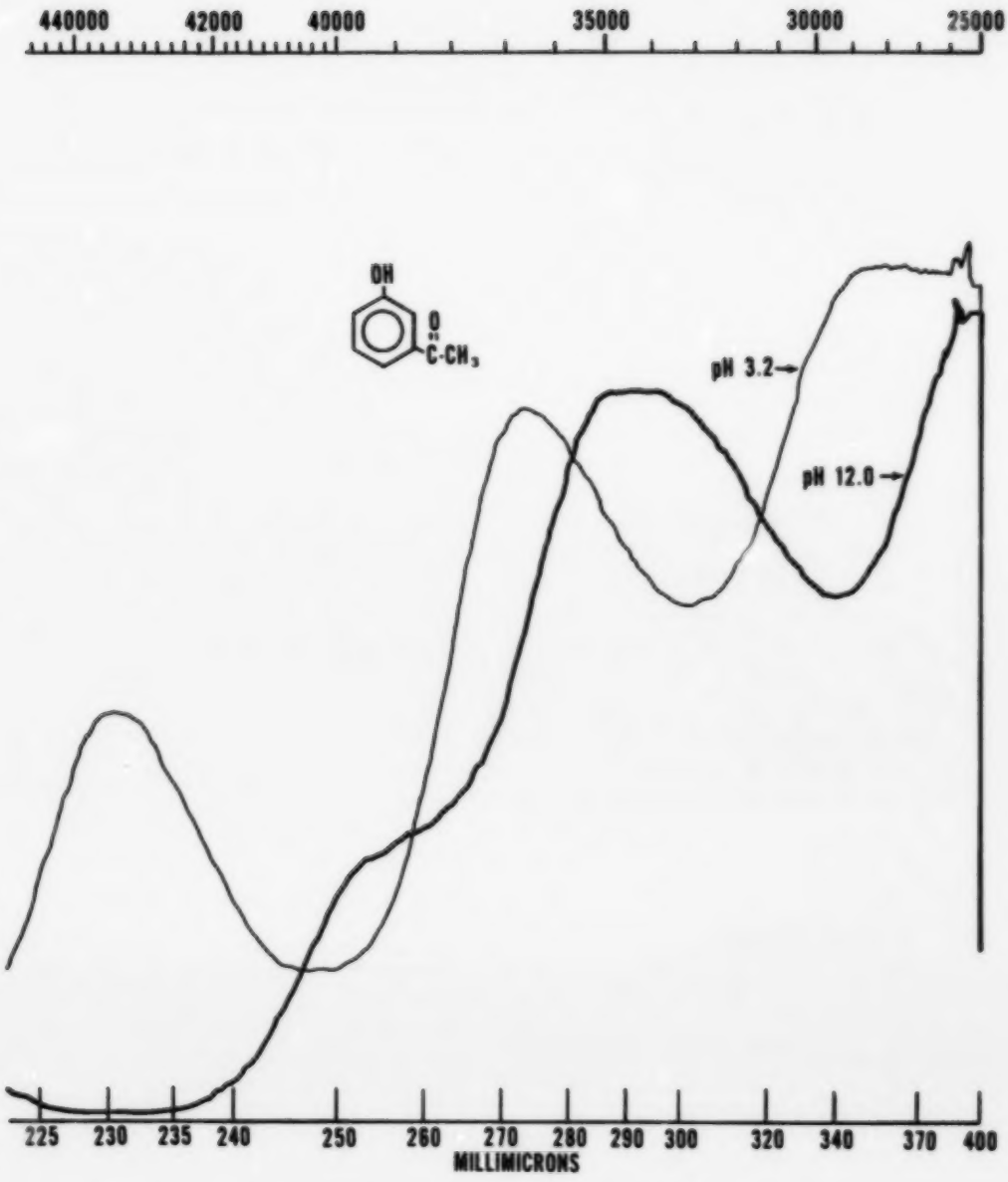

FIGURE 6. 3-HYDROXYACETOPHENONE